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# Martian Airglow

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Without doubt the study of airglow in the terrestrial atmosphere has been and still is an important approach to the study of the upper atmosphere. It therefore seems natural to inquire whether observable airglow from other planets, such as Mars and Venus, would be expected to occur, based, of course, on our present knowledge of the composition of these planetary atmospheres. It is not the purpose of this paper to present a discussion of the various model atmospheres that have been proposed for these planets, but rather to present an airglow mechanism which can be expected to occur on Mars and Venus. The implications of this airglow will be discussed only for the Martian atmosphere, although they should also apply to Venus.

Let us assume that the Martian atmosphere is composed of 2 per cent $CO_2$ and the remainder $N_2$, the surface pressure being about 100 mb (Grandjean and Goody, 1955). The density distribution of these constituents with altitude should be somewhat similar to that of the earth. Thus, at some altitude corresponding to unit optical depth for solar radiation shortward of 1700 Å, where $CO_2$ absorbs (Inn, Watanabe and Zelikoff, 1953), we expect the following photodissociation process,

$$CO_2+h\nu \rightarrow CO+O. \tag{1}$$

If we assume some sort of photochemical equilibrium at these altitudes, then the important reactions which follow are:

$$CO+O+M \rightarrow CO_2+M \tag{2}$$

$$O+O+M \rightarrow O_2+M \tag{3}$$

$$O_2+O+M \rightarrow O_3+M \tag{4}$$

$$O_3+O \rightarrow 2O_2, \tag{5}$$

where M refers to any other atom or molecule, principally however, to $N_2$.

The reaction (2) has been the subject of a number of investigations (Clyne and Thrush, 1962; Mahan and Solo, 1962) and, in fact, is commonly associated with the CO flame emission. Thus, in essence, reaction (2) is a chemiluminescent recombination reaction with a characteristic complex banded spectrum due to $CO_2$ between about 5000–3000 Å, the maximum intensity being at about 4000 Å. Although there appears to be some question as to the kinetics and mechanism of the recombination, it is clear that the emission is due to electronically excited $CO_2$.

Since the over-all recombination reaction is spin forbidden,

$$CO(^1\Sigma)+O(^3P) \rightarrow CO_2(^1\Sigma_g^+) \tag{6}$$

the following scheme has been proposed for the chemiluminescent reaction (Clyne and Thrush, 1962):

$$CO(^1\Sigma^+)+O(^3P) \rightarrow CO_2(^3B_2), \tag{7}$$

$$CO_2(^3B_2) \rightarrow CO_2(^1B_2) \text{ (radiationless)}, \tag{8}$$

$$CO_2(^1B_2) \rightarrow CO_2(^1\Sigma_g^+)+h\nu, \tag{9}$$

that is, the flame bands are due to an allowed transition. Note that $^3B_2$ and $^1B_2$ refer to excited $CO_2$ in bent configuration derived, respectively, from $^3\Delta u$ and $^1\Delta u$ in the linear molecule. We also note that (9), $^1B_2 \rightarrow {}^1\Sigma_g^+$, is an allowed transition; hence, the emission should be fairly intense. However, the actual rate of emission appears to be controlled by a potential maximum in the $^3B_2$ state and the probability of radiationless transition to the neighboring $^1B_2$ state.

Clyne and Thrush (1962) measured $I$, the absolute emission rate of (2), and found that

$$I=I_0(CO)(O), \tag{10}$$

where $I_0$ is independent of the total pressure (measured

over a pressure range of 0.9–3 mm Hg), depending only on the nature of $M$. The temperature dependence of $I_0$ over the range 200–300K appeared to give a positive activation energy of about 3700 kcal per mole which is probably related to the potential maximum in the $^3B_2$ state. If we now take the measured value of $I_0$ for $T=293$K, $M=N_2$, $\lambda=3200$–$5000$ Å, and express $I$ in units of photons cm$^{-3}$ sec$^{-1}$, we have

$$I=1.9\times10^{-20}(\mathrm{CO})(\mathrm{O}), \qquad (11)$$

where (CO) and (O) are expressed in molecules cm$^{-3}$.

Although the above results were obtained for total pressures in the range 0.9 to 3 mm Hg, we will apply (11) to the Martian atmosphere with, for illustrative purposes, the assumed conditions (CO) = (O) = $10^{12}$ cm$^{-3}$ and a 1 cm$^2$ column of 10 km length. Thus, the apparent emission rate, $I'$, is given by

$$I'=1.9\times10^{10} \text{ photons cm}^{-3} \text{ sec}^{-1} (10^6 \text{ cm column})$$
$$=19 \text{ kilorayleighs (kR)}.$$

The apparent brightness at zenith over the sunlit Martian atmosphere would then be

$$B=1.5\times10^{9} \text{ photons cm}^{-3} \text{ sec}^{-1} \text{ sterad}^{-1}.$$

Such an intense Martian airglow, although probably just beyond detection from the Earth, should be readily measured from any fly-by probe. Clearly, such a measurement could be related to the total amount of CO and O in the Martian atmosphere.

It should be noted that the above calculations refer to airglow emission above any presumed layer of $O_2$, which, by virtue of the Schumann-Runge absorption continuum, would effectively screen $CO_2$ at lower altitudes, thus preventing further photodissociation of the latter (Chamberlain, 1962). This screening effect is most pronounced in the terrestrial atmosphere and it is estimated that this source of airglow on the Earth would be about $10^{-5}$ of that calculated for Mars.

If we now assume larger concentrations of CO and O, we note that the apparent brightness rapidly approaches values which should be readily observable from the earth. In fact, it is quite conceivable that the brightness of the blue airglow may be an important factor in reducing the general contrast in this region of the spectrum in the Martian atmosphere, for example, blue haze. Thus, in blue light the observed "reflection" may be, in reality, partly reflected sunlight and partly airglow, the latter being indistinguishable from the former, and hence, may contribute measurably to the observed albedo of about 0.05 (de Vaucouleurs, 1959). The extent of haziness (e.g., clearing) may then be due to the airglow emission rate being controlled both by temperature, through the activation energy, and change in CO and O concentrations. However, no explanation as to how these changes occur can be offered at this time. We also note that any spectral features which may appear as discrete absorption bands in the blue haze may well be reinterpreted as due to discrete band emission. For example, under low dispersion the regions between band maxima in the blue CO flame emission spectrum may take on the appearance of absorption bands in the absence of other identifiable features in the spectrum. Of course, it is not intended, in the preceding discussion, to minimize the possible importance of molecular scattering and pure absorption in being responsible for the observed phenomenon.

We now consider the variation of the intensity across the disk of Mars in blue light. Clearly, in view of the greater depth of the emitting region at the limb of the disk, we should observe limb brightening if the blue airglow contributes appreciably to the albedo. Of course, the degree of limb brightening will depend on the optical depth of airglow radiation in the Martian atmosphere.

The only ultraviolet (2700 Å) albedo measurement of Mars reported so far is that published by Boggess and Dunkelman (1959) who obtained a value of 0.24. If we assume the latter value as reasonably correct, then it would seem that the Martian airglow could be an explanation of this apparently large value of the ultraviolet albedo. Although no observations of the CO flame emission have been reported for wavelengths shortward of 3000 Å, it is expected that the chemiluminescence does extend into the ultraviolet region with perhaps somewhat lower intensity compared to that at the maximum at 4000 Å. On the other hand, the solar intensity of 2700 Å is about $\frac{1}{10}$ that at 4000 Å. The contribution of any ultraviolet airglow from the sunlit Mars could result in the measurement of a relatively large apparent albedo.

It must be admitted that the above discussion of the implications of the blue Martian airglow is rather speculative; however, it is certain that the airglow does exist. It, therefore, remains to be corroborated by probe observations. Further laboratory experiments are also needed to establish the absolute rate of emission of the CO flame spectrum.

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